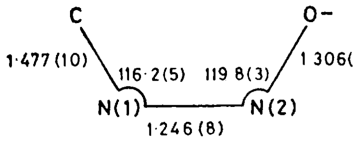
Crystallographic Determination of the *cis*-Configuration of *syn*-Disodium 4-Sulphonatobenzenediazotate

By **Nathaniel W. Alcock,* Paul D. Goodman,** and **Terence J. Kemp,*** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

The crystal structure of the title compound has been determined at −150 °C from diffractometer data by the heavy-atom method. The crystals were orthorhombic, space group $Pna2_1$, with unit cell dimensions a = 5.559(1), b = 11.699(4), c = 19.371(4) Å, $\alpha = \beta = \gamma = 90°$, Z = 4 and R = 0.062 for 838 observed reflections. The *syn*-diazotate group was found to have a *cis*-configuration, making a dihedral angle of 69.1(13)° with the benzene ring. The bond lengths for C(4)–N(1), N(1)–N(2), and N(2)–O(4) are 1.455(15), 1.296(13), and 1.318(11) Å, respectively. The anions, cations, and water molecules are extensively linked in a three-dimensional network.

THE debate about the structures of the two different forms of the arenediazotates has a long and celebrated history, and the controversy as to whether the ' normal ' or ' *syn* ' form and the ' *iso* ' or ' *anti* ' form are geometrical or structural isomers has been described at length.[1,2] While it is now universally accepted [3,4] that the two forms are indeed geometrical isomers, the assignment of the *syn*-form as *cis* and the *anti*-form as *trans*, initially due to Hantzsch,[5] was based on analogy with similar compounds and on kinetic data. The lack of more substantive structural evidence led Sterba *et al.*[6] to propose, on the basis of the effect of *ortho*-substituents on the rate and equilibrium constants of the isomerization reaction that, in contrast to accepted opinion, the *anti*-diazotates have the *cis*-configuration.

Previously, the only crystal structure available has been that of the aliphatic salt *syn*-potassium methanediazotate (A).[7]



(A)

As well as this information for an aliphatic diazotate, i.r. data [8] have indicated that the bond order of N(1)–N(2) is greater than that of the N–O bond, and that *syn*-diazotates possess a non-planar, distorted *cis*-structure.

In view of the absence of definitive crystallographic material relating to the aromatic diazotates, which would finally resolve the debate, we have undertaken a low-temperature crystal-structure determination of *syn*-disodium 4-sulphonatobenzenediazotate. From a considerable series of diazotates, this was the only one for which suitable crystals could be prepared.

EXPERIMENTAL

Materials.—The title compound was prepared following LeFevre *et al.*,[9] 4-sulphonatobenzenediazonium chloride being made by the inverted method.[10] Sulphanilic acid (8.5 g) and sodium nitrite (3.5 g) were dissolved in water (60 cm^3) and the arenediazonium salt precipitated on addition of concentrated HCl (5.5 cm^3). The yellow solid was filtered off and washed with water. The still damp product was mixed with an equal weight of crushed ice and stirred with 40% sodium hydroxide solution (80 cm^3) to obtain a lemon-yellow solution. Colourless needles separated over 12 h at 0 °C. These were filtered and washed with small quantities of methanol (yield 3.2 g). Microanalysis indicated a stoicheiometry $C_6H_4N_2Na_2S,3H_2O$.

Structure Determination.—The small needle-shaped crystals were found to decompose at room temperature in the X-ray beam. However, by cooling the crystal to −150 °C using a Syntex LT-1 attachment, this problem was overcome. Unit cell dimensions and data were collected using a Syntex $P2_1$ four-circle diffractometer, with a graphite monochromator. The small crystal size required that the initial orientation photograph was given only a partial rotation, and that all reflection centring was performed at slow speed.

Crystal Data.—$C_6H_4N_2Na_2O_4S,3H_2O$, M = 348, orthorhombic, a = 5.559(1), b = 11.699(4), c = 19.371(3), U = 1 259.9 Å^3, D = 1.30 g cm^{-3}, Z = 4, Mo-K_α radiation, λ = 0.710 69 Å, $F(000)$ = 616, −150 °C. Accurate cell constants were obtained by means of least-squares calculations based on the positions of 15 reflections. The systematic absences, $0kl$, $k + l \neq 2n$ and $h0l$, $h \neq 2n$, indicates either $Pna2_1$ or $Pnam$ as the space group. The latter would require either m or $\bar{1}$ symmetry for the molecule, and as these seemed unlikely, the non-centrosymmetric space group was provisionally selected and shown to be correct by refinement. Since a very small, weakly diffracting crystal was used, data were collected slowly to achieve satisfactory accuracy. Reflections were measured, using θ–2θ scans over a scan range of ± 0.8 to a maximum 2θ of 45°. A variable scan rate of 0.5—29° min^{-1} was used, depending on the intensity of a preliminary 2 s count. Background counts were recorded at the end of each scan for an equal time to the scan. 1389 reflections were collected, of which 838 were considered observed $I/\sigma(I) \geqslant 3.0$ and used in final refinement. Lorentz and polarisation corrections were applied, but not an absorption correction.

A Patterson synthesis revealed the position of the sulphur atom and Fourier methods were used to locate all the non-hydrogen atoms. Anisotropic temperature factors were used for the sulphur and sodium atoms in the last stages of least-squares refinement. Hydrogen atoms were not considered. The refinement converged to a final R of 0.062, with unit weights for all reflections.

Computing was carried out with the SHELX program on a Burroughs B6700 computer. The final co-ordinates are listed in Table 1, interatomic bond lengths and angles in Table 2, and skeletal torsional angles in Table 3. Anisotropic temperature factors and final structure factors are listed in Supplementary Publication No. SUP 22761 (6 pp.).*

DISCUSSION

The molecule is found to have the predicted structure [8] with the *syn*-diazotate group in a *cis*-configuration. The dimensions of the sulphonate group are almost identical to those in benzenediazonium-4-sulphonate,[11] although the benzene ring is less distorted. This would be expected as the diazotate group is a much weaker electron-withdrawing substituent than the diazonium group. Kübler and Lüttke [8] predicted from i.r. studies of a series of substituted arenediazotates that the *syn*-arenediazotate has a non-planar structure and, by comparison with compounds with isoelectronic groups, that the diazotate group is *cisoid* and is distorted in some unspecified way. The C(4)–N(1) bond makes a slight angle (5.5°) with the plane of the ring, and the diazotate group (itself being planar) has a dihedral angle of 69.06 (13)°: with the ring plane. Comparison with *syn*-potassium methanediazotate [7] showed significant differences, *i.e.* (i) N(1)–N(2) and N(2)–O(4) in the title compound are fairly similar, 1.296(13) and 1.318(11) Å, respectively, whereas in the aliphatic diazotate they are substantially different, 1.246 (8) and 1.306(7) Å, respectively. This indicates more extensive delocalisation for the title compound. Thus (B) is a better representation than (C). (ii) The angle C(4)–N(1)–N(2) (119.3°) in the present compound is significantly closer to pure sp^2 than in the aliphatic diazotate (116.2°), whereas the angles N(1)–N(2)–O(4) are fairly similar (118.8 and 119.8°).

TABLE 1

Atomic co-ordinates of the bonded atoms (with standard deviations in parentheses)

Atom	*X*	*Y*	*Z*
S	0.500 9(5)	0.556 9(2)	0.500 0(0)
O(1)	0.355 3(12)	0.454 0(6)	0.498 4(4)
O(2)	0.730 8(13)	0.544 4(6)	0.465 2(4)
O(3)	0.366 5(13)	0.657 7(6)	0.477 4(4)
O(5)	0.632 6(13)	0.678 7(6)	0.333 9(4)
O(6)	−0.342 3(14)	0.297 5(6)	0.401 7(4)
O(7)	0.349 9(20)	0.194 5(9)	0.704 3(6)
C(1)	0.577 3(19)	0.576 5(9)	0.589 2(5)
C(2)	0.422 5(20)	0.536 4(9)	0.640 1(6)
C(3)	0.487 9(19)	0.552 3(9)	0.710 1(5)
C(4)	0.707 4(19)	0.604 7(8)	0.726 2(6)
C(5)	0.857 1(20)	0.645 9(9)	0.674 6(6)
C(6)	0.794 8(20)	0.632 5(9)	0.605 2(6)
N(1)	0.775 1(17)	0.632 2(8)	0.796 8(5)
N(2)	0.822 9(16)	0.550 0(7)	0.839 5(5)
Na(1)	−0.007 3(7)	0.382 0(3)	0.453 9(2)
Na(2)	0.993 7(8)	0.667 7(3)	0.405 4(2)
O(4)	0.807 8(14)	0.443 6(6)	0.817 6(4)

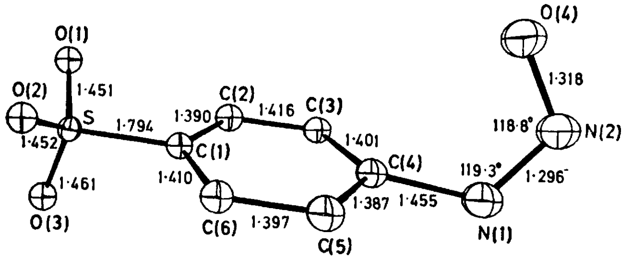


FIGURE 1 ORTEP view of *syn*-disodium 4-sulphonatobenzenediazotate down *a*

TABLE 2

Interatomic bond lengths (Å) and angles (°) (with standard deviations in parentheses)

Bond lengths			
S–C(1)	1.794(10)	C(3)–C(4)	1.401(15)
S–O(1)	1.451(7)	C(4)–C(5)	1.387(16)
S–O(2)	1.452(8)	C(5)–C(6)	1.397(16)
S–O(3)	1.463(8)	C(4)–N(1)	1.455(15)
C(1)–C(2)	1.390(15)	N(1)–N(2)	1.296(13)
C(1)–C(6)	1.410(15)	N(2)–O(4)	1.318(11)
C(2)–C(3)	1.416(15)		
Bond angles			
O(1)–S–C(1)	105.0(5)	C(5)–C(4)–C(3)	121.0(10)
O(2)–S–C(1)	104.6(5)	C(6)–C(5)–C(4)	120.3(10)
O(3)–S–C(1)	107.8(5)	C(3)–C(4)–N(1)	122.1(10)
C(2)–C(1)–C(6)	122.1(10)	C(4)–N(1)–N(2)	119.2(9)
C(3)–C(2)–C(1)	118.4(10)	N(1)–N(2)–O(4)	118.8(9)
C(4)–C(3)–C(2)	119.6(10)		

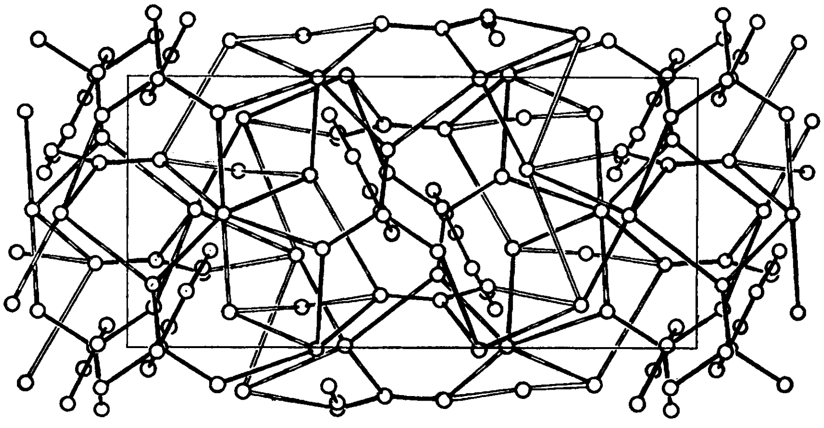


FIGURE 2 Packing diagram for *syn*-disodium 4-sulphonatobenzenediazotate viewed down *c*. Key to bonding type: open lines, hydrogen bonds; filled lines, covalent bonds; dashed lines, co-ordination to Na^+ ions

Crystal Packing.—The anions, cations, and water

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* For details see Notices to Authors No. 7, in *J.C.S. Perkin II*, 1979, Index issue.

molecules are extensively bonded to give a rigid three dimensional structure (Table **4**). Na(1) is five co-ordinated to O(1), O(2), and N(2) of the anion, and also to two O(6) water molecules. Na(2) is six co-ordinated to O(2), 0.3, O(3), and O(4) of the anion, and to two O(5) water molecules. The N(1)–O(6) distance [2.830(12)] indicates the presence of a hydrogen bond. The O(6) water molecules are also connected to each other in a chain throughout the structure by probable hydrogen bonds. Similarly, the O(4) atom of the anion is doubly hydrogen-bonded to water molecules O(5) and O(7).

TABLE 3

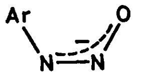
Skeletal torsional angles (°) (with standard deviations in parentheses)

C(3)–C(4)–N(1)–N(2)	69.1(13)
O(1)–S–C(1)–C(2)	−28.6(10)
O(2)–S–C(1)–C(2)	−148.2(9)
O(3)–S–C(1)–C(2)	91.2(9)
C(2)–C(3)–C(4)–N(1)	174.6(9)
C(6)–C(5)–C(4)–N(1)	−174.2(9)

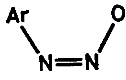
TABLE 4

Intermolecular and interionic distances (Å) (with standard deviations in parentheses)

Sodium co-ordination			
Na(1)–O(1)	2.349(8)	Na(2)–O(3)	2.501(8)
Na(1)–O(6)	2.338(9)	Na(2)–O(3)	2.573(8)
Na(1)–O(6)	2.505(8)	Na(2)–O(4)	2.410(9)
Na(1)–O(2)	2.404(8)	Na(2)–O(5)	2.442(9)
Na(1)–N(2)	2.568(10)	Na(2)–O(5)	2.397(8)
Na(2)–O(2)	2.358(8)		
Hydrogen bonding			
N(1)–O(6)	2.830(12)	O(4)–O(5)	2.853(11)
O(6)–O(6)	2.994(11)	O(4)–O(7)	2.735(14)
O(5)–O(7)	2.918(14)		



(B)



(C)

Finally, there is a hydrogen bond between O(5) and O(7).

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